1.0

4.5
5.0
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2.8
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2.5

2.2

1.1

2.0

1.8

1.25 1.4 1.6

MICROCOPY RESOLUTION TEST CHART

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HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

The Boranes and Their Relatives.

William N. ~~Limscomb~~ LIPSCOMB

12 *Oxford Street*
Cambridge, Massachusetts 02138
U.S.A.

22 March ~~20,~~ 1977

Re: Final Report on Office of Naval
Research Contract N00014-76-C-0199

Final rept. 1 April ~~1,~~ 1968 - 31 January ~~31,~~ 1977

Office of Naval Research (Code 472)
Arlington, Virginia 22217

Dear Sirs:

I cannot think of a more suitable document than the manuscript which I submitted to the Nobel Foundation for publication in their forthcoming volume "Les Prix Nobel en 1976."

Sincerely yours,

William N. Lipscomb
Abbott and James Lawrence Professor
of Chemistry

L:G

The Boranes and Their Relatives

by William N. Lipscomb

Harvard University, Cambridge, Massachusetts, U.S.A.

This year, 1976, the Nobel Prize in Chemistry has been awarded for research in pure inorganic chemistry, in particular the boranes. May I say that I am most pleased and profoundly grateful. My own orientation to this field has been, as it has in all of my studies, the relationships of the chemical behavior of molecules to their three-dimensional geometrical and electronic structures. The early work on the molecular structures of boranes by X-ray diffraction led to a reasonable basis for a theory of chemical bonding different from that which is typical in carbon chemistry, and yielded an understanding of the pleasing polyhedral-like nature of these compounds. Assimilated by the preparative chemists, the principles helped to establish a large body of a hitherto unknown chemistry, which made a reality of the expectation that boron, next to carbon in the periodic table, should indeed have a complex chemistry.

In these nearly thirty years both the theoretical and experimental methods have been applied by us and others to areas of inorganic, physical, organic and biochemistry. For examples, these areas include low temperature X-ray diffraction techniques, and the theoretical studies of multicentered chemical bonds including both delocalized and localized molecular orbitals. An early example is extended Hückel theory, originally developed for studies of the boranes, and even now one of the most widely applicable approximate methods for theoretical studies of bonding in complex molecules. More soundly based theories are presently in use by my research students for studying how enzymes catalyze reactions, details of which are based on the three-dimensional structures by X-ray diffraction methods. Besides illuminating particular problems, these developments may contribute toward the redefinition of areas of chemistry, and thereby broaden the chemist's view. Our research in the boranes and their related molecular species crosses areas of inorganic, experimental physical, theoretical and organic chemistry, and includes applications in biochemistry. More simply stated, the area is the study of the relationships of molecular structure to function.

Boranes, and Early Structure Studies

By now, large numbers of chemical compounds related to polyborane chemistry exist: boron hydrides, carboranes, metalloboranes, metallo-carboranes, mixed compounds with organic moieties, and others. These discoveries of preparative chemists are relatively recent. Long ago, Alfred Stock established borane chemistry. He developed the experimental techniques which were required for the preparation of the volatile and potentially explosive compounds, B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} and B_6H_{10}, and the relatively stable white crystalline $B_{10}H_{14}$. This work, beautifully summarized in his Baker Lectures,[1] was celebrated at the Third International Meeting on Boron Chemistry this past July in Munich, 100 years after his birth. Sidgwick[2] wrote, "All statements about the hydrides of boron earlier than 1912, when Stock began to work on them, are untrue."

Aside from the classification as either an N+4 or an N+6 series, no simple basis for these unusual formulas was foreseen before their structures were established. A B_6 octahedron (Fig. 1) was known in certain crystalline borides, and the B_{12} icosahedron (Fig. 2) was found in boron carbide, but no one realized that a systematic description of the boron arrangements in these hydrides might be based on fragments of these polyhedra. Most electron diffraction work before 1940 supported more open structures, which Pauling[3] described in terms of resonating one-electron bonds. In 1940-1941 Stitt[4] produced infrared and thermo-dynamic evidence for the bridge structure of B_2H_6 (Fig. 3). More general realization of the correctness of this structure followed the theoretical studies,[5-8] and especially the infrared work of Price.[9] The three-center bridge BHB bond was clearly formulated by Longuet-Higgins.[8]
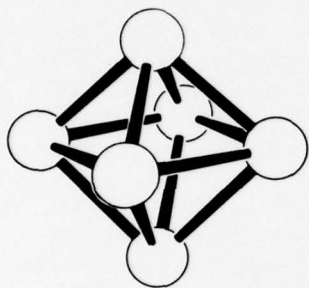

Fig. 1. The B_6 octahedron, which occurs in certain metal borides, in which each boron atom is bonded externally to a boron atom of another octahedron. In $B_6H_6^{-2}$ or $C_2B_4H_6$, a terminal hydrogen atom is bonded externally to each B or C atom.
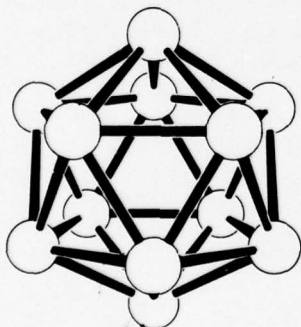

Fig. 2. The B_{12} icosahedron, which occurs in boron carbide $B_{12}C_3$, in elementary boron, and in $B_{12}H_{12}^{-2}$. The three isomers of $C_2B_{10}H_{12}$ also have this icosahedral arrangement in which there is one externally bonded hydrogen on each B or C atom.
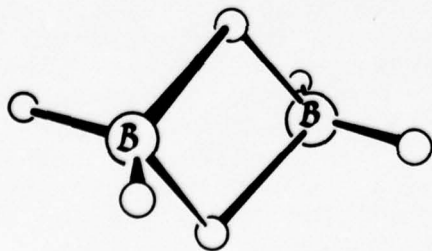

Fig. 3. The geometrical structure of B_2H_6.

The first of the higher hydrides to be characterized structurally was $B_{10}H_{14}$ (Fig. 4). Kasper, Lucht and Harker[10] showed that the boron arrangement was a fragment of a B_{12} icosahedron in which there are four bridge BHB bonds in the open face. Next was B_5H_9[11,12] (Fig. 5), a fragment of the B_6 octahedron, and then B_4H_{10}[13,14] (Fig. 6), a B_4 unit from these polyhedra. Both of these structures were established by X-ray diffraction in our laboratory, and by electron diffraction at the California Institute of Technology. Our X-ray diffraction results on
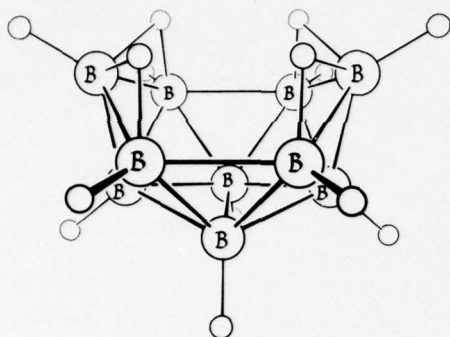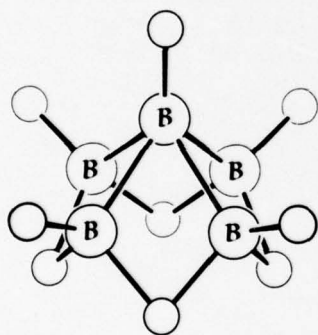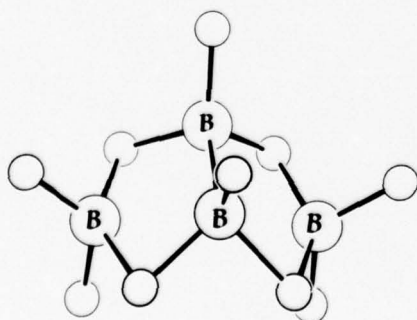

Fig. 4. $B_{10}H_{14}$.

Fig. 5. B_5H_9.

Fig. 6. B_4H_{10}.

B_5H_{11}[15] (Fig. 7) and tetrahedral B_4Cl_4[16] then set the stage for the beginning of the theory of bonding. The B_6H_{10} structure,[17,18] (Fig. 8) completing the compounds found by Stock, was to be one of our later X-ray diffraction studies, which were to include many other boranes and related molecules.

It was actually in 1946 that I decided to enter this area of inorganic chemistry. At that time, no reliable methods were generally available for accumulation of large amounts of X-ray diffraction data. Our methods[19] paralleled those in Fankuchen's laboratory[20] at the then Polytechnic Institute of Brooklyn, but were quite independent. Because of the special difficulties of working with the volatile boranes, I chose among other topics, a series of X-ray diffraction studies of single crystals grown at low temperatures from low melting liquids for which probable residual entropy problems existed: N_2O_2, CH_3NH_2, CH_3OH, N_2H_4, $COCl_2$ and H_2O_2. The subsequent low temperature studies of single crystals of these volatile and unstable boranes were not without hazards. Vacuum line techniques were learned as we needed them. Fortunately, no serious injuries were incurred as a result of several explosions resulting from cracks in these vacuum systems. I was relieved, on one occasion, when I had taken Russell Grimes to a hospital in Cambridge after one of these explosions to hear the doctor tell me, "Louis Fieser sends me much more interesting cases than you do." I still have in my office the air gun which I, or my young son, used on a number of occasions to destroy a cracked vacuum system from a safe distance. We also had chemical surprises, for example, when we found a presumed B_8 hydride to be B_9H_{15}.[21] Our only chemical analysis of this compound was the count of the numbers of boron and hydrogen atoms in the electron density map, which was calculated in those days from rough visual estimates of intensities of diffraction maxima on films.
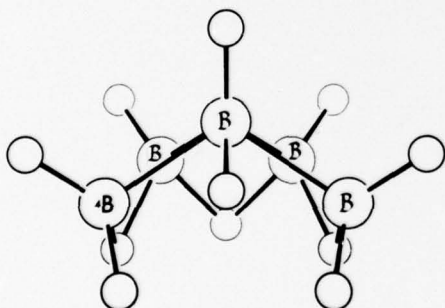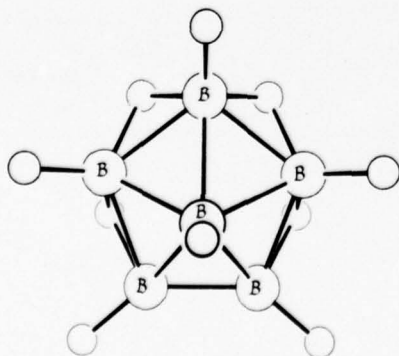

Fig. 7. B_5H_{11}.

Fig. 8. B_6H_{10}.

Three-Center Bonds Among Boron Atoms

At the fortunate time in 1953 of W. H. Eberhardt's sabbatical, he, Crawford and I examined[22] the open boron hydrides B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} and $B_{10}H_{14}$ from the viewpoint of three-center bonds; and we studied B_5H_9, the unknown polyhedral molecule B_4H_4, the then hypothetical ions $B_6H_6^{-2}$ (Fig. 1) and $B_{12}H_{12}^{-2}$ (Fig. 2) from the viewpoint of molecular orbitals. Longuet-Higgins[23] also, independently, formed an early molecular orbital description almost like ours. One of the simple consequences of these studies was that electron deficient molecules, defined as having more valence orbitals than electrons, are not really electron deficient. I mean by this non-sequitur that the three-center two-electron bonds make possible a simple description of these molecules and ions as filled orbital species. Filled molecular orbitals were later extended to closed polyhedral compounds B_nH_n for all values of n from 5 to 24, all of which have a formal charge of -2, even though hypothetical B_4H_4 is neutral. In fact, all of the experimentally known ions, for $6<n<12$, do have -2 charge. In addition to $B_6H_6^{-2}$ (Fig. 1) and $B_{12}H_{12}^{-2}$ (Fig. 2), those polyhedra for $5<n<10$ are shown in Fig. 9. The isoelectric series $C_2B_{n-2}H_n$ is known for $5<n<12$.

Equations for the atom, orbital and electron balance were formulated in our paper of 1954, allowing prediction of many new chemical species. One simple form of these rules is exemplified for a neutral hydride formula B_pH_{p+q} in which each boron atom has at least one terminal hydrogen atom. Define the number of BHB bridges as s, the number of three-center BBB bonds as t, the number of two-center BB bonds as y and the number of extra terminal hydrogens on each BH unit as x. Then

$$s + x = q$$
$$s + t = p$$
$$p = t + y + q/2$$

The first equation is the hydrogen balance. The second comes from the fact that each of the p boron atoms supplies four orbitals and only three electrons, and the extra orbital is utilized in one of the two types of three-center bond. Finally, if each BH unit is recognized as contributing a pair of electrons, these p pairs are used in BBB or BB bonds, or in half of the pairs required for the extra terminal hydrogens. These rules, and the accompanying valence structures, are especially helpful in describing those polyboron compounds which are open, but they are also useful for closed polyhedral molecules and ions.
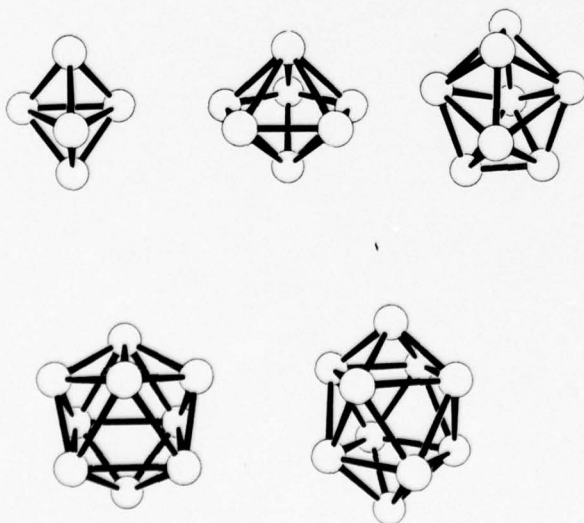

Fig. 9. Structures for the boron and carbon arrangements in some of the polyhedral molecules $C_2B_{n-2}H_n$, which are known for $5<n<12$. The isoelectronic anions are known for $6<n<12$.

There are two kinds of three-center bonds among three boron atoms (Fig. 10). The central three-center bond involves positive overlap among hybrid orbitals from each of three boron atoms, while the open three-center bond involves, on the central atom, a π orbital which overlaps in a bonding manner with an orbital from each of the adjacent boron atoms. The less compact B_2H_6, B_4H_{10}, B_5H_{11} and B_6H_{10} structures (Figs. 11-14)
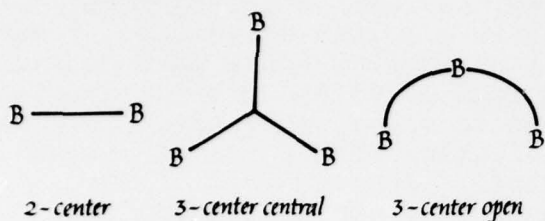

Fig. 10. The three types of bonds within the boron framework of a borane structure, or an equivalent carborane structure, are a BB bond, and the two types of three-center bonds. As shown below, the open three-center bond is known only for BCB bonds, not BBB bonds.
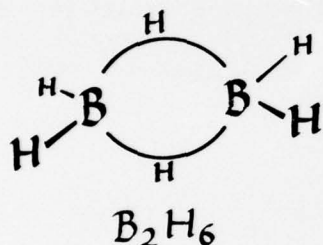

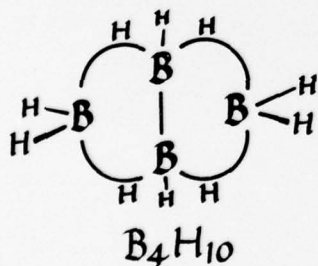Fig. 11. Bonds in B_2H_6, according to three-center bond theory.
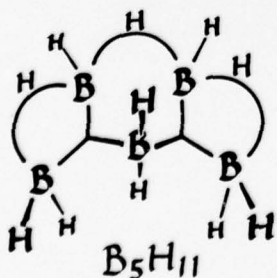

Fig. 12. Bonds in B_4H_{10}.

Fig. 13. Bonds in B_5H_{11}.

are well described with the use of these three-center bonds, omitting
open three-center BBB bonds for the moment. However, B_5H_9 (Fig. 15)
requires a resonance hybrid of four valence structures, related by the
four-fold symmetry; and $B_{10}H_{14}$ (Fig. 16) requires a resonance hybrid
of 24 valence structures.

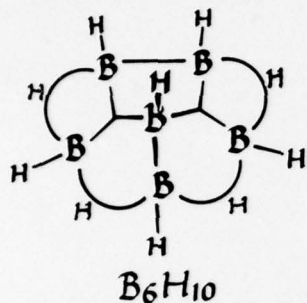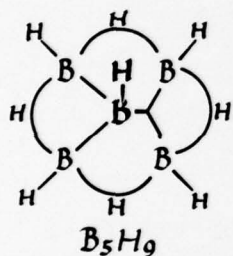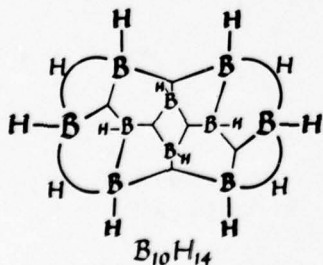B_6H_{10}

Fig. 14. Bonds in B_6H_{10}.

B_5H_9
One of 4 resonance forms

Fig. 15. One of the four resonance structures
for B_5H_9. The other three are obtained by
reorientation of the framework bonds by 90°
about the molecular four-fold axis.

$B_{10}H_{14}$
One of 24 resonance forms

Fig. 16. One of the 24 resonance structures
for $B_{10}H_{14}$, omitting open three-center bonds.

Three-center bond theory was further developed in the following 22 years.[24] I realized that the valence rules implied the existence of a large body of boron chemistry, and then ventured predictions, some of which were actually verified experimentally. Dickerson[25] and I formalized my intuitive approach into a theory of connectivity of various bonding patterns within the three-center description. Also, geometrical constraints were introduced in order to avoid overcrowding of hydrogen atoms and to preserve known bonding angles about boron atoms among the boranes.[26] More recently, Epstein[27] and I reformulated the topology using central three-center BBB bonds, to the exclusion of open three-center BBB bonds. The recent work on localized molecular orbitals which has led to the restriction of open three-center bonds, so far, to BCB bonds is exemplified in a later part of this manuscript.

Molecular Orbital Studies of Boranes

Molecular orbitals are more appropriate for describing the valence structures of the polyhedral molecules and ions, and the more compact polyhedral fragments. Two simple examples will suffice. In B_5H_9 there are three pairs of electrons in the boron framework, which has four-fold symmetry. The bonding is beautifully described, without resonance, by a simple σ and π set of molecular orbitals[22,24,28] (Fig. 17). These orbitals are similar to the bonding orbitals, for example, between planar four-fold cyclobutadiene (C_4H_4) and a CH^+ placed along the four-fold axis to give the carbonium ion $C_5H_5^+$.

A similar σ,π situation occurs[28] if a BH unit is removed from icosahedral $B_{12}H_{12}^{-2}$ leaving $B_{11}H_{11}^{-2}$ having five atomic orbitals containing four electrons (Fig. 18). This set of five orbitals gives σ,π molecular orbitals which can bond to a similar set of σ,π orbitals from another atom or group of atoms supplying two more electrons. I suggested, conceptually, adding H_3^+ to predict $B_{11}H_{14}^-$, for example.

MO's in B_5H_9
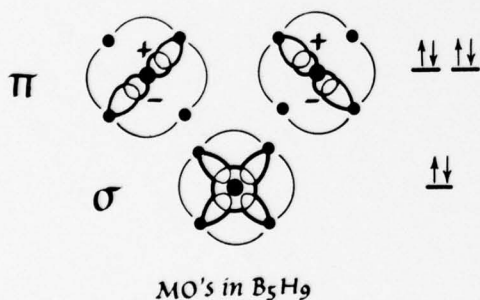
Fig. 17. Symmetry molecular orbitals in the boron framework of B_5H_9. The σ molecular orbital is a five-centered one, and each of the π components is actually an open three-center bond.

Five AO's to apex in $B_{12}H_{12}^{-2}$

Fig. 18. Five atomic orbitals, containing four electrons when a neutral BH unit is removed from the apex of $B_{12}H_{12}^{-2}$, or $C_2B_{10}H_{12}$. These five atomic orbitals form a σ(bonding), π(bonding) and δ(antibonding) set of five molecular orbitals, like those in the π electron system of $C_5H_5^-$.

Although recognizing the similarity of this set of orbitals to those in C_5H_5, which was known to form ferrocene $Fe(C_5H_5)_2$, I did not then go quite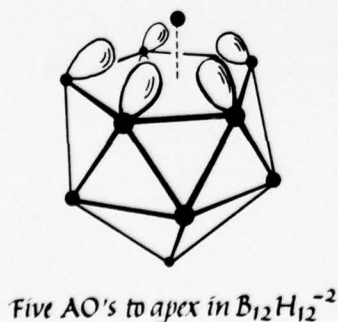 so far as to suggest bonding of this $B_{11}H_{11}^{-2}$ fragment to a transition metal. Later, Hawthorne did so, using these ideas as a starting point, and thereby created the large family of metalloboranes and metallocarboranes[29] (Fig. 19).

In the early 1960's, when large scale computing facilities became available to us, Roald Hoffmann and Lawrence Lohr independently programmed the extended Hückel method in my research group. Its first application was to boron chemistry,[30] where, particularly in the carboranes (compounds of boron, carbon and hydrogen), the charge distributions predicted sites of electrophilic and nucleophilic substitution. One of the rather simple rules which emerged was that nucleophilic attack occurs in a polyhedral carborane at a boron atom closest to carbon, while electrophilic attack was preferred at a boron furthest removed from carbon. Experimental studies of boranes and carboranes in which one or more hydrogens had been replaced by a halogen or by an amine group confirmed these predictions. The extended Hückel method became for a time the most widely used program for the study of molecular theory and reactions in complex organic and inorganic molecules. For example, the Woodward-Hoffmann rules, and related orbital concepts, were tested by their inventors[31] with the use of this theory.

I thought then that progress in structure determination, for new polyborane species and for substituted boranes and carboranes, would be greatly accelerated if the [11]B nuclear magnetic resonance spectra, rather than X-ray diffraction, could be used. One approach was empirical,[32] while the other was purely theoretical. This latter approach required the development of a theory for fairly reliable calculation of chemical shifts of [11]B from first principles of quantum mechanics.[33] This theory, the coupled Hartree-Fock method for a molecule in a magnetic or electric field, yielded molecular constants good to a few to several percent[34] for many diatomic molecules. A striking result was the prediction of the paramagnetic nature of diatomic BH.[35] However, the application of this method to the complex boranes still lies in the future, even after 13 years of effort. While we understand some of the contributions to chemical shift, diamagnetic and large temperature-independent paramagnetic effects, the use of this method for structure determination of complex polyboranes is still somewhat limited.

These programs yielded accurate self-consistent field molecular orbitals, which were explored in other areas of chemistry, as well as in the boranes and carboranes. One example is the first accurate calculation of the barrier to internal rotation in ethane.[36] At this point, my research students and I set out to explore the gap between extended Hückel theory and self-consistent field theory. We achieved by stages[37,38]
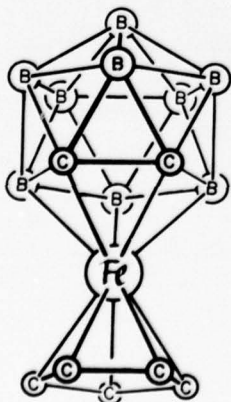

Fig. 19. The structure of $(B_9C_2H_{11})Fe(C_5H_5)$, a metallocarborane derivative.

a molecular orbital theory[39] still being extended, which was applicable to large polyboranes and other molecules, and which had essentially the accuracy of self-consistent field methods. Molecular orbital methods which do not go beyond symmetry orbitals tend to make each molecule a separate case. Hence we began only a few years ago to explore the connections between these symmetry orbitals and the three-center bonds of the previous section.

Localized Molecular Orbitals

Ordinarily, molecular orbitals are classified according to their symmetry types. However, it is possible to make linear combinations of molecular orbitals of different symmetries in such a way that the total electron density of the molecule remains invariant. The most popular methods are those of Edmiston and Ruedenberg[40] who maximize

$$\sum_i \int\int \phi_i(1)\phi_i(1) \ \frac{1}{r_{12}} \ \phi_i(2)\phi_i(2) dV_1 dV_2$$

and of Boys[41] who minimizes

$$\sum_i \int\int \phi_i(1)\phi_i(1) r_{12}^2 \phi_i(2)\phi_i(2) dV_1 dV_2$$

These procedures, respectively, maximize the repulsions of those electron pairs within each molecular orbital, and minimize the orbital self-extension of each electron pair. Thus, in slightly different manner, the symmetry orbitals are converted into linear combinations which are a good approximation to the localized electron-pair bond. These objective procedures, without adjustable parameters, have been compared in some detail.[42] They provide support of three-center bond descriptions within a theoretical chemical framework. Also, they test the level at which two-center and three-center bonds require some further delocalization. These studies have also provided preferred descriptions of valence structures, often eliminating or reducing the need for resonance hybrids.

Open three-center and central three-center BBB bonds are almost equivalent descriptions. Including both types there are 111 resonance structures for $B_{10}H_{14}$, of which 24 are based only on central three-center bonds. In B_5H_{11} (Fig. 20) two slightly unsymmetrical central three-center BBB bonds are found[43] by both localization procedures (Fig. 20c), whereas the open three-center description is not favored. In a series of studies
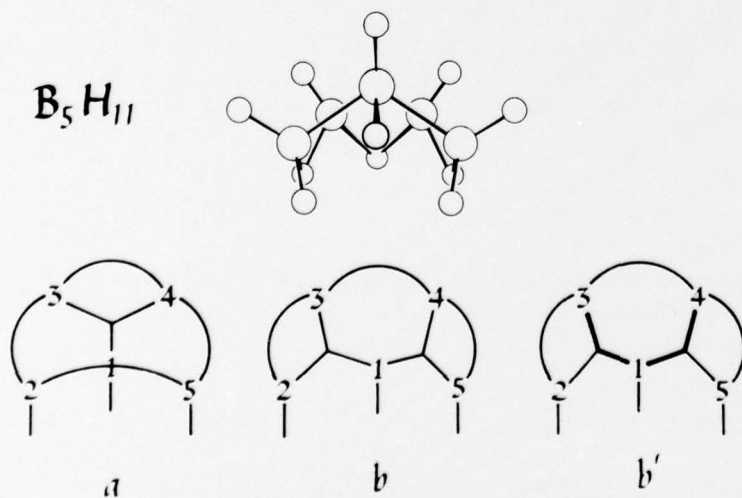

B_5H_{11}

Fig. 20. Three valence structures of B_5H_{11} include (a) the disfavored open three-center bond, (b) the symmetrical central three-center bonds, and (b') the localized slightly unsymmetrical three-center bonds. For clarity, one terminal B-H bond has been omitted at each boron site in (a), (b) and (b').

of localized molecular orbitals in all of the boron hydrides, carboranes, and ions of known geometry, we have never found an open three-center BBB bond. However, open three-center BCB bonds do exist. For example, the open three-center BCB bond[44] occurs twice in $1,2-C_2B_4H_6$ (Fig. 21), when the Edmiston-Ruedenberg procedure is used. A comparison of these results with those of the Boys procedure is given below. In the simplest molecular orbital description of an open three-center bond, the electron pair is distributed as e/2, e, e/2 among these three atoms. It is probable that the extra nuclear charge of carbon stabilizes this distribution, to give open three-center bonds rather than nearly equivalent central three-center bonds, when carbon is the middle atom.

Another new general result is that almost every single bond within a triangulated borane or carborane framework shows some donation to the nearest adjacent atoms (Fig. 22). This tendency for multi-centered bonding usually involves 10 per cent or less of the electron pair. In B_4H_{10}, about 0.2 e is donated[43] from the single BB bond to each of atoms B_1 and B_4, which themselves are relatively electron deficient because of the open three-center bonds of the hydrogen bridges (Fig. 23). This donation then causes these hydrogen bridges to become unsymmetrical, displaced toward B_2 and B_3, in accord with the results obtained from our X-ray diffraction
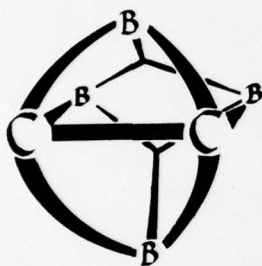

Fig. 21. Localized molecular orbitals are shown in the framework of $1,2-C_2B_4H_6$. The open three-center bonds go through carbon. An external hydrogen has been omitted at each B or C atom.
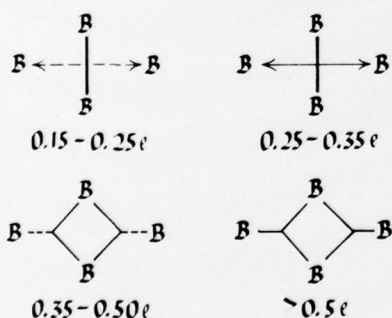

Fig. 22. Notation is shown for amounts of single bond donation to adjacent boron atoms. Unsymmetrical donation may also occur.
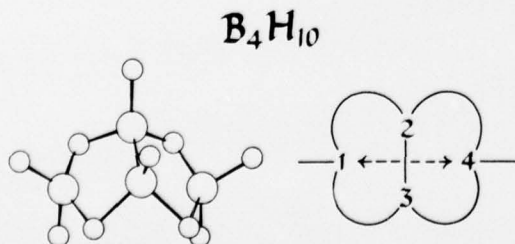

Fig. 23. Single bond donation in B_4H_{10} is about 0.19e from the B_2B_3 bond to each of the outer doubly bridged BH_2 groups of the molecule.

study. More generally, this donation causes electron withdrawal along other bonds in the molecule, whether or not hydrogen bridges are available for accommodating this electron displacement. Two additional examples are illustrated in $B_8H_{13}^-$ and in the predicted structure of B_8H_{14}, respectively[45] (Fig. 24 and 25). I have abstracted from these examples some typical modes of single bond donation, and accompanying electron withdrawal or hydrogen displacement, in Fig. 26. These and similar valence diagrams may be useful in understanding intramolecular distortions and reaction mechanisms.
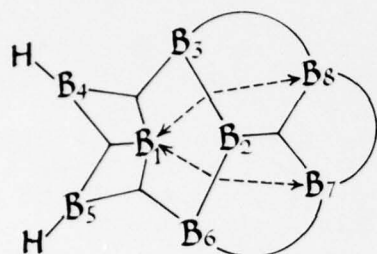

Fig. 24. Single bond donation is shown in $B_8H_{13}^-$.
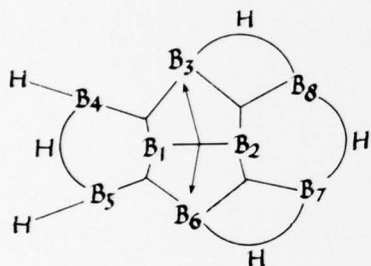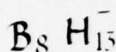

Fig. 25. Donation occurs from the B_1B_2 single bond in B_8H_{14}.
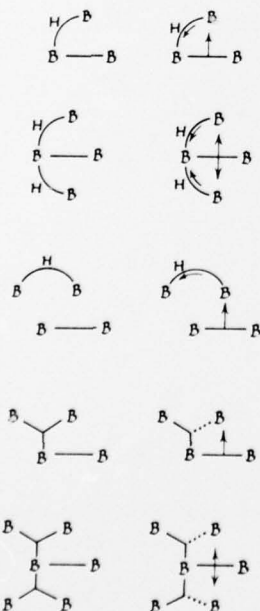

Fig. 26. Some common patterns of single bond donation cause hydrogen atom displacement and electron withdrawal from the atom to which donation occurs.

A new type of bonding, which is conceptually transferable among these molecules, is described as fractional three-center bonds.[46] Its simplest interpretation is the replacement of a pair of resonance structures by a single valence structure (Fig. 27). The fractional use of orbitals, indicated by dotted lines, increases the apparent number of bonds to a given boron above the usual four, for an element in the first row of the periodic table. However, the Pauli exclusion principle is not violated because less than a full atomic orbital is required at a fractional bond. Indeed, the localized molecular orbitals are themselves derived from wavefunctions for which the exclusion principle is rigorously introduced. The use of fractional bonds to reduce the number of resonance hybrids, often to a single preferred structure, is not limited to boranes and their relatives. Our rather extensive studies of bonding among atoms other than boron have indicated that these simplified localized molecular orbitals may be an informative and useful alternative to the more conventional valence bond and molecular orbital descriptions in other parts of the periodic table. A very simple example, carboxylate anion,[47] is shown in Fig. 28.

Fractional bonds to atom B_2 in $4,5-C_2B_4H_8$ are preferred[48] over a resonance hybrid of a single and a central three-center bond, and also are preferred over the open three-center bond (Fig. 29). Also, the bond-
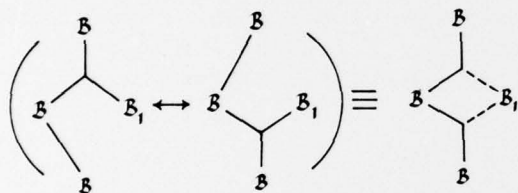
Fig. 27. Equivalence is shown of the two fractional three-center bonds to a resonance hybrid of a single bond and a three-center bond.
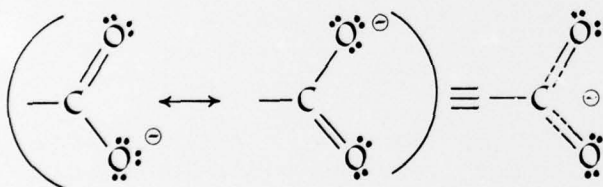

Fig. 28. The four localized molecular orbitals in carboxylate anion have a charge distribution which shows displacement toward oxygen. On the left, the equivalent resonance hybrid is given.
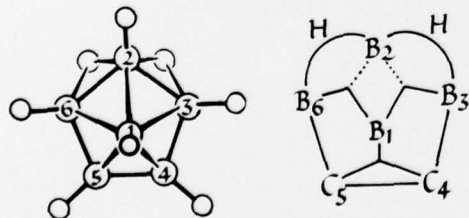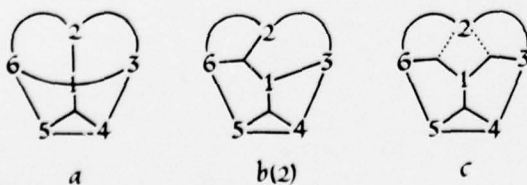
$4,5-C_2B_4H_8$

Fig. 29. Localized orbitals in $4,5-C_2B_4H_8$ show fractional donation to atom B_2 as dotted lines.

ing of the two carbon atoms in this carborane by both a single bond and a central three-center bond has not been found in boranes, and, in particular, does not occur in B_6H_{10} which is isoelectronic with $4,5\text{-}C_2B_4H_8$. Fractional bonds give a particularly simple valence description[45] of bonding in $B_{10}H_{14}$ (Fig. 30), where the single valence structure (Fig. 30c) replaces a resonance hybrid of 24 central three-center bond structures. A very similar simplification[45] occurs in $B_{10}H_{14}^{-2}$, where the two pairs of fractional bonds are dotted toward atoms B_2 and B_4, rather than toward B_6 and B_9.

Similar pairs of fractional bonds are found by Boys' localization procedure in the polyhedral carboranes $1,2\text{-}C_2B_4H_6$ (Fig. 31) and $1,7\text{-}C_2B_{10}H_{12}$ (Fig. 32). Perhaps this procedure tends to exaggerate the separation of charge centroids of bonds when they lie at or near a single
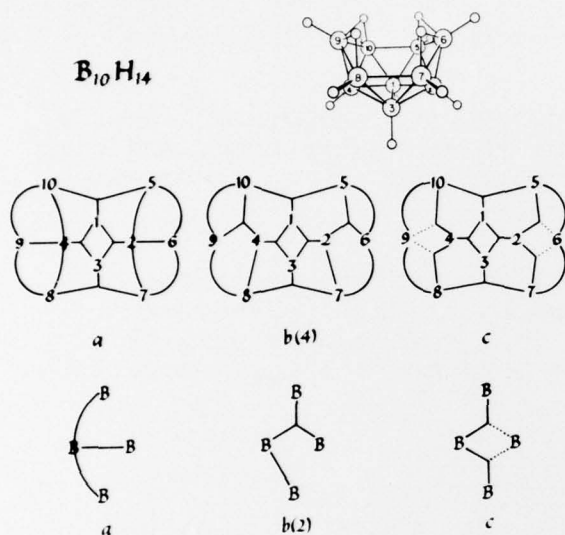
$B_{10}H_{14}$

Fig. 30. The pattern of fractional bonds, dotted toward B_6 and B_9, in $B_{10}H_{14}$ can be expected when there is resonance of the type shown in the central diagram, or when one is tempted to draw open three-center BBB bonds as shown on the right. The fractional bond description is preferred.
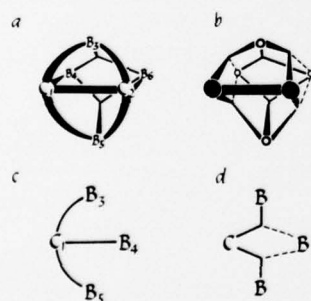
Fig. 31. In $1,2\text{-}C_2B_4H_6$ the Edmiston-Ruedenberg localization yields open three-center bonds at carbon, while the Boys localization gives fractional three-center bonds. The latter procedure gives greater emphasis to separation of orbital centroids when they are on the same atom.
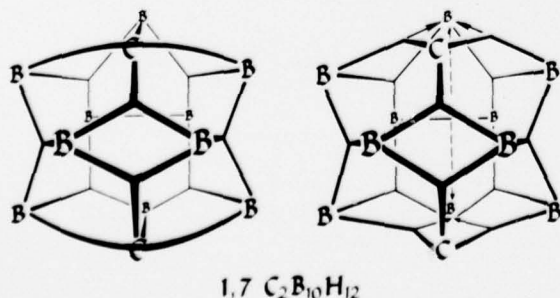
$1,7\ C_2B_{10}H_{12}$

Fig. 32. A situation parallel to that of Fig. 31 may occur in $1,7\text{-}C_2B_{10}H_{12}$, where the Boys localization (right side) shows fractional bonds. The open three-center bond description may be found by the Edmiston-Ruedenberg procedure, if and when the calculations can be made.

center. For this reason, we tend to prefer[42] the almost equivalent open
three-center bonds, as found by the Edmiston-Ruedenberg procedure in
$1,2-C_2B_4H_6$. When it becomes economically feasible to test this alternative
in $1,7-C_2B_{10}H_{12}$, I would guess that localized open three-center bonds
will be found, centered at carbon atoms, in this molecule, like those in
$1,2-C_2B_4H_6$.

Fractional three-center bonds are not always unique, particularly
in aromatic hydrocarbons, or in those boranes which have a valence
pattern similar to that in the aromatics. An example of this orienta-
tional ambiguity occurs in the boron framework bonds in B_5H_9 (Fig. 33).
Actually, the two valence structures represent extremes over a 45° range
of orientation angle, about the four-fold axis. There is a continuum
of valence structures between these extremes. Moreover, this ambiguity
continues throughout the whole 360°, in accord with the four-fold
symmetry which the electron density must have in this molecule. All of
these valence structures are equally preferred, and each has a total
electron density which is consistent with the four-fold molecular
symmetry.

In more complex molecules one can find various degrees of simplicity
in the bonding patterns of localized molecular orbitals. In $C_2B_{10}H_{13}^-$,
which has a somewhat open near-icosahedral C_2B_{10} arrangement, the bonding
is especially simple,[49] not requiring resonance or appreciable fractional
bonding (Fig. 34). In $1,2-C_2B_{10}H_{12}$, another simple idea occurs: the
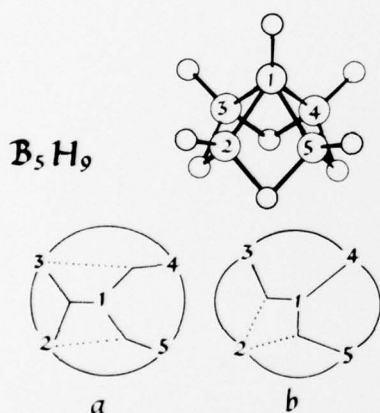

B_5H_9

Fig. 33. There is an orientational
ambiguity about the four-fold axis of
B_5H_9 involving a continuum of valence
structures between (a) and (b), and
extending eventually throughout the
complete 360° range.
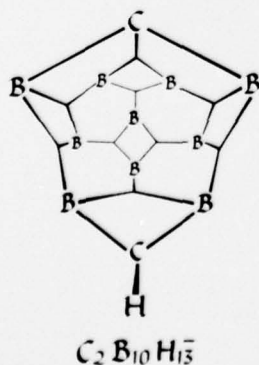
$C_2B_{10}H_{13}^-$

Fig. 34. There is little fractional bonding
in the localized orbitals of the nearly
polyhedral $C_2B_{10}H_{13}^-$ ion.

bonding, as found by Boys' procedure, is to a good approximation just like that in $1,7-C_2B_{10}H_{12}$ in spite of the very different positions of the two carbon atoms relative to each other and to their boron neighbors (Fig. 35). Thus there is some tendency for bonding invariance in closely related geometrical structures. In iso-$B_{18}H_{22}$, we find[50] both single bond donation, from B_4B_8 and $B_{14}H_{18}$, and fractional bonds, to B_6 and B_{16} (Fig. 36). Here, the single bond donations are greater toward B_9, which is relatively electron deficient, than toward B_3 and B_{13}.
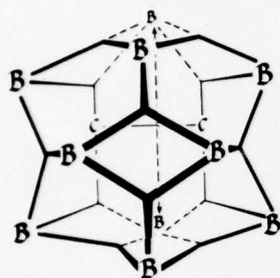
1,2 $C_2B_{10}H_{12}$

Fig. 35. The localized orbitals obtained for $1,2-C_2B_{10}H_{12}$ by Boys procedure are the same as those found in $1,7-C_2B_{10}H_{12}$ in spite of the differences in positions of carbon atoms relative to boron atoms.
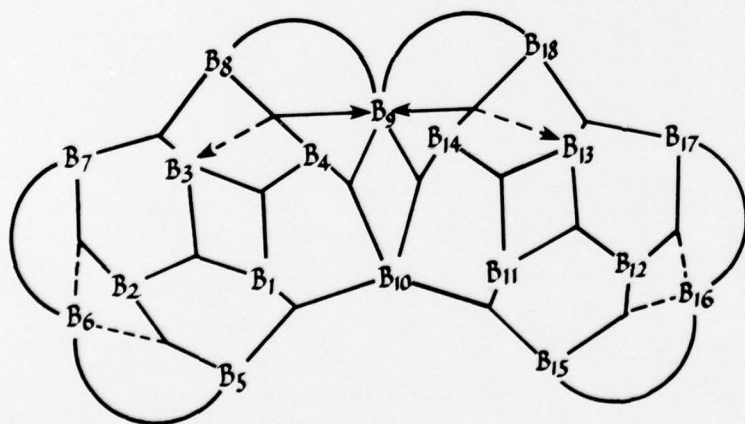
Fig. 36. Single bond donation and fractional bonds occur in iso-$B_{18}H_{22}$, a molecule having a two-fold axis only, and no terminal hydrogen atoms on B_9 and B_{10}.

In $B_{20}H_{16}$ there is a remarkable amount of single-bond donation, particularly toward the electron deficient B_9———B_{16} atoms, inclusive (Fig. 37), and the valence structure of each half is clearly like that in $B_{10}H_{14}{}^{-2}$ (Fig. 38) rather than like that in $B_{10}H_{14}$ (Fig. 30).
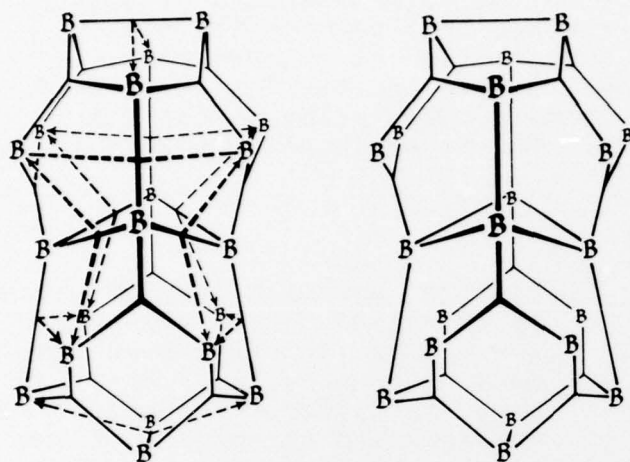
$B_{20}H_{16}$

Fig. 37. Donation and non-donation localized orbitals are shown for $B_{20}H_{16}$, in which the four borons nearest the equatorial belt have no terminal hydrogens. Boron atoms B_9-B_{15}, inclusive, are particularly electron deficient, and receive substantial dona-tion from single bonds.
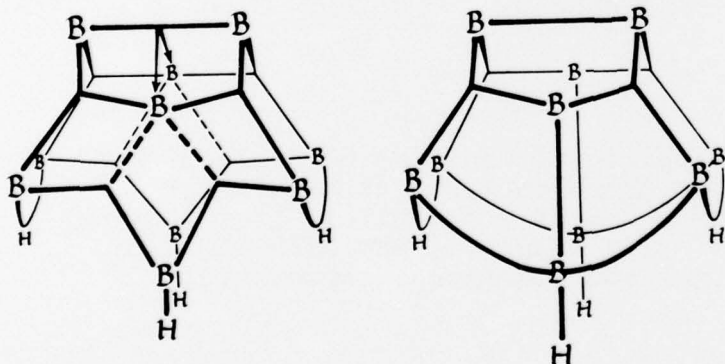
$B_{10}H_{14}^{=}$ (LMO's) $B_{10}H_{14}^{=}$ (open)

Fig. 38. A relationship similar to that in $B_{20}H_{16}$ occurs in $B_{10}H_{14}{}^{-2}$. The preferred localized orbital structure is shown on the left side, while the open three-center bond struc-ture without donation is an oversimplified valence structure.

The rather complex localized molecular orbitals in $B_{16}H_{20}$ (Fig. 39) are dominated by the three-center bond approximation; in addition they are modified by single bond donation accompanied by electron withdrawal from atoms to which donation occurs.[50] With recognition that atoms B_9 and B_{10} have no terminal hydrogens attached to them, I offer the reader a challenge to find the close relative valence structures which do not have fractional bonding or single bond donation in this molecule.

Finally, the bonding in reaction intermediates is a new area of study, primarily by purely theoretical methods. In BH_5 (Fig. 40) there is only a very weak donor bond from H_2 to the vacant orbital of BH_3.[51-55] This weakness is probably due to the absence of a pathway for back donation. On the other hand, in the dimerization of two BH_3 molecules to form B_2H_6, donation of electron density from one terminal H to B of the other BH_3 group is balanced by a symmetrically related donation toward the first BH_3 group[56] (Fig. 41). Our other recent progress in
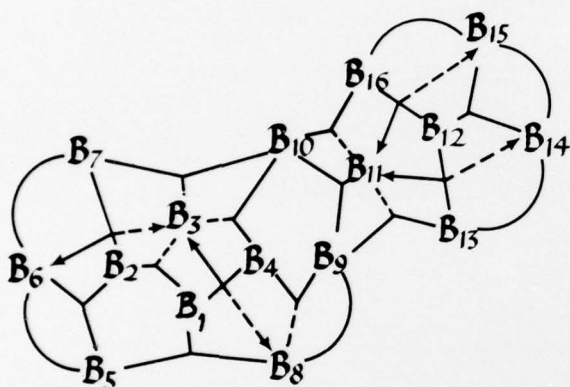
$B_{16}H_{20}$

Fig. 39. A rather complex pattern of localized orbitals is shown for $B_{16}H_{20}$. Bond donations can be withdrawn by the reader in order to discover the preferred valence bond structures of the simpler theory. This single valence structure replaces a resonance hybrid of 216 valence structures based upon central three-center bonds and single bonds. Atoms B_9 and B_{10} do not have terminal hydrogens.
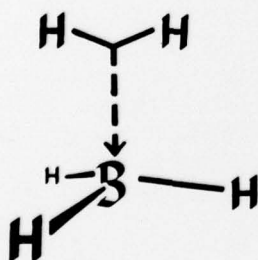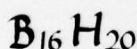
Fig. 40. Fractional donation of a single bond between two hydrogen atoms to the vacant orbital of a slightly pyramidal, nearly planar, BH_3 group. The resulting BH_5 molecule is a very short-lived reaction intermediate.
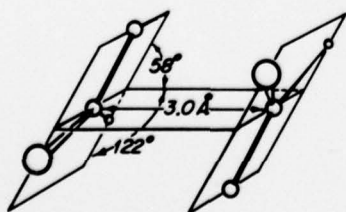
Symmetry C_{2h}

Fig. 41. Approximate geometry of the transition state when two BH_3 molecules form B_2H_6. This geometry is favored over that in an unsymmetrical approach of two BH_3 molecules.

theoretical studies of bonding in reaction intermediates, such as B_3H_7 and B_4H_8,[57] shows that the more stable transient species may have a vacant orbital on one boron atom, because of the strain involved when that vacant orbital is filled by converting a terminal BH bond to a bridge BHB bond. Actually less is known of the detailed reaction mechanism for reactions of boranes and their related compounds than is known for organic reactions of comparable complexity. Surely, this is a fruitful area for future research.

I shall stop here, omitting descriptions of bonding in large poly-hedral borane anions and other related compounds. Also, polyhedral rearrangements, hydrogen atom tautomerism, and particularly the use of bonding theory in bringing some degree of order to chemical transforma-tions of the boranes have been omitted. Attention has thus been con-centrated on those aspects of chemical bonding which have been especially illuminated by the molecular and crystal structures that we and others have studied over these many years.

It remains to give credits where they really belong, to my research associates: graduate students, undergraduates, postdoctoral fellows and my other colleagues who have coauthored nearly all of these studies. For the figures of this manuscript, and of the lecture, I thank Jean Evans. I am most grateful to the Office of Naval Research who supported this research during the period from 1948 to 1976, a remarkably long time. I am most aware of the great influence of Linus Pauling on my whole scientific career. Finally, this manuscript is dedicated to the memory of my sister, Helen Porter Lipscomb, composer, teacher and performer.

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